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GOODYEAR AEROSPACE CORPORATION

AKRON 15, OHIO

RIGIDIZED INFLATABLE SOLAR ENERGY CONCENTRATORS

by

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GER-11318

FIRST MONTHLY PROGRESS REPORT,

COVERING PERIOD FROM 30 SEPTEMBER ~~1963, THROUGH~~ 31 OCTOBER 1963

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I. INTRODUCTION

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This first monthly progress report covers the work accomplished from 30 September through 31 October 1963. Two major areas were pursued during this period:

(1) Reviewing and developing various azide structures

(2) Locating and contracting an azide synthesizing firm

A number of azide structures have been reviewed, and a number of preliminary investigations have been performed to learn more of the physical properties of the azides and their resulting polyurethane foam products. The approach of reducing peak temperatures by control of rate-of-decomposition of the azide and rate-of-gelation of the polyurethane foam has been pursued. Progress in these areas are discussed below. The location of an azide supplier required more time than expected, but results have been obtained and progress is expected to speed up as the program continues.

A program schedule, a schedule forecast of manpower utilization, and a schedule forecast of fund expenditures are also presented. Actual cost figures are submitted separately as requested.

AUTHOR

II. GENERAL

This project has as its objective the production of a rigid polyurethane foam from ingredients which may be pre-mixed and pre-distributed over a surface without reaction, by virtue of one or more ingredients being inert when mixed. The pre-distributed mixture must not react in storage and yet be capable of activation by limited heating. When activated in a vacuum environment, a low density, high strength foam should result.

The primary reactants in a polyurethane foam are polyesters and polyethers with reactive hydrogen in the molecule, ordinarily as pendant hydroxyl groups, and another compound having two or more isocyanate groups (-NCO) per molecule.

The basis of the present effort is the prior finding in Goodyear Aerospace Laboratories that certain acid azides may be employed as the inert ingredient specified above. When exposed to slightly elevated temperatures, such acid azides undergo a reaction (Curtius rearrangement of the $-CON_3$ acid azide group to the -NCO group) which produces reactive isocyanates and which also liberates molecular nitrogen that can serve as the necessary blowing gas.

Within the framework of the above objective, it is necessary to search for the best choices of foam reactants and reactant ratios to yield a controllable, operable process under acceptable conditions of temperature, pressure and time that are compatible with the environment of an earth orbit. The foam produced must in turn meet certain requirements in physical properties and compatibility with other structural components.

III. APPROACH

The areas of investigation presently in view are briefly summarized below. They are interrelated but are arbitrarily classed here as related to the process or to the product.

A. Process

1. Choice of Azide -

It is necessary to prepare in a laboratory the acid azides of di- or higher functionality that are potentially useful in the process; so far as is known, none are commercial materials at present. The desirable properties in an azide may be stated as:

a. The undergoing of the Curtius rearrangement smoothly and quantitatively in the temperature range of about 150-200° F in a few hours or less. A lower activating temperature is undesirable since it would create storage problems. (Various azides, mostly mono-functional, are reported in the literature to rearrange at temperatures from 60 to 300° F; side reactions may limit isocyanate yield to 80% or so.)

b. A low heat release from the rearrangement of the azide would be desired since exothermic reactions may lead into overheating.

c. The isocyanate resulting from the azide rearrangment should probably be a fast reacting compound.

d. It is, of course, necessary to ensure the release of a sufficient amount of nitrogen blowing gas, by formulating with at least a minimum amount of contained azide group per unit weight of total mixed ingredients. If larger percentages of the azide group are required to yield sufficient isocyanate for the polymerization process, the additional nitrogen release brings on complications not encountered in the usual foam systems.

e. Physical state at room temperature to be a liquid that would mix readily with other viscous liquid ingredients.

f. Very low vapor pressure of both the azide and its isocyanate rearrangement product to prevent loss of either prior to or during the foaming process.

g. On the basis of chemical principles and a limited number of past observations, there is some reason to believe that a part or all of the azide material could advantageously be of tri- or higher functionality.

2. Choice of Polyester and/or Polyether Resin -

A considerable variety of polyether resins and a somewhat limited number of polyester resins are available from commercial sources. Properties of these materials that will affect processing include:

a. Functionality or the average number of hydroxyl groups per molecule and also molecular weight. These combined give average equivalent weight, which is another index of structure and aids in setting up another criterion of the product; i.e., molecular weight per cross link.

b. The proportion between primary and secondary hydroxyl groups will affect reactivity. Primary hydroxyls would be expected to be faster reacting.

c. The room temperature viscosity of the resin may be expected to control the viscosity of the mixed ingredients that are to be pre-distributed on a film substrate. Obviously, neither very liquid nor semi-solid mixtures would be desirable. The viscosity and surface tension when activation temperature is first reached will influence the early stages of foam swell.

d. Very low vapor pressure would be advantageous.

e. High solvent power for the azide co-reactant would be highly desirable if it permitted having all ingredients in a single phase.

f. Very low water content of these generally hygroscopic resins would be advantageous.

3. The Choice and Use of Auxiliary Ingredients -

Auxiliary ingredients such as surface active agents and catalysts for the polymerization reaction will require consideration. We have no indication, unfortunately, that the Curtius rearrangement is susceptible to catalysis. The sensitization of acid azides to shock or temperature by impurities has been little studied and we infer it is not a catalytic process in the usual sense.

B. Products

1. The physical properties of strength and high softening temperature that are desired will require a high density of cross links (low equivalent weights for both isocyanate and polyol plus complete reaction).

2. The structure of the moieties between cross links will be determined, of course, by the structures of the azides and polyol reactants. Indications are that azides containing a high percentage of aromatic rings will contribute to a stiff polymeric structure. Likewise in the polyol (polyester or polyether resin) aromatic or heterocyclic character may be advantageous.

IV. EXPERIMENTAL WORK ACCOMPLISHED DURING THIS REPORTING PERIOD

A. Experimental Materials

Foaming studies have employed terephthaloyl azide (Structure I), a Plaskon polyester resin PFR-6 and prepolymer derived from this resin plus an isocyanate terminated prepolymer (also containing free tolylene diisocyanate) with the trade designation Glidfoam PCR 5043. Known properties of the resins are shown in Table I. Table II contains information on azide Structure I, and also lists other azides that have been synthesized in the previous GAC program.

B. Foaming Studies

In past work employing PFR-6 polyester resin, it has seemed advantageous to build molecular weight of the resin by reacting (approximately 2 hours at about 210 - 240° F) 10 parts PFR-6 with 2.3 parts by weight (pbw) of Glidfoam PCR-5043. This yields a tacky semi-solid material (prepolymer) with 21% (calculated) of the resin hydroxyl groups reacted assuming an average hydroxyl number of 480. The theoretical azide requirement (as terephthaloyl azide) would then be one part prepolymer to 0.59 parts azide (37% azide in the total mix). In order to reduce the exothermic heat of the azide rearrangement and to assure better utilization of diisocyanate from azide, it has seemed desirable to make trials of the following:

1. The reduction of the azide component from the 37% (equivalence) value to 20% leaving excess hydroxyl groups in the final foamed polymer (which may reduce loss of diisocyanate). Such foams formed at atmospheric pressure have a polymer melt temperature of 170-180° F.

2. The reaction of a higher percentage of the PFR-6 hydroxyl groups in forming the prepolymer. Work is in progress with prepolymer made with 2.8 pbw Glidfoam RCR-5043 to 10 pbw PFR-6. Viscosities and densities for these prepolymers are reported in Table I.

C. Measurement of Heat Release From Azide Rearrangement

Preliminary experimentation is underway on this subject.

D. Azide Synthesis

An effort to synthesize in three steps 2,6-naphthalene diacyl azide Structure VI, Table III from an available compound, the dimethyl ester of 2,6-naphthalene dicarboxylic acid, has been continued under the contract. A satisfactory product from the first step has been taken through the second step, and inspection of the second product to determine if it is of reasonable purity is underway. In addition, a contract has been let to synthesize three additional azide compounds; these are Structures X, XI, XII as shown in Table III.

TABLE I

PROPERTIES OF EXPERIMENTAL MATERIALS

PLASKON PFR-6

	Manufacturer's Data	Lab Measurement
Acid No.	15-20	14
Hydroxyl No.	465-495	538
Brookfield Visc. 25°C(cp)	70,000-80,000	65,500
Water Content %	0.0-0.4	0.83
Desnity g/cc	-	1.15

GLIDFOAM RCR 5043

	Manufacturer's Data	Lab Measurement
Amine Equivalent	123:1	126
Hydrolyzable Chlorine	0.009	--
Density g/cc	-	1.21

Prepolymer From 10 pbw PFR-6 + 2.3 pbw Glidfoam RCR 5043

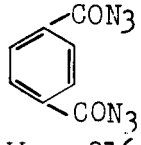
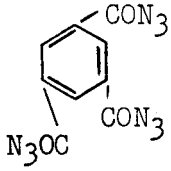
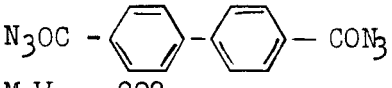
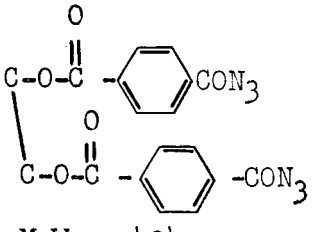
	Brookfield Viscosity			Density
Temp. (°F)	194	212	230	g/cc
cp.	49,500	25,000	14,500	1.2

Prepolymer From 10 pbw PFR-6 + 2.8 pbw Glidfoam RCR 5043

	Brookfield Viscosity				Density
Temp. (°F)	194	212	230	284	g/cc
cp.	> 100,000	85,000	55,000	8,500	1.18

TABLE II

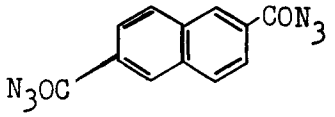
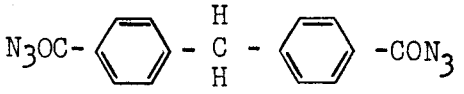
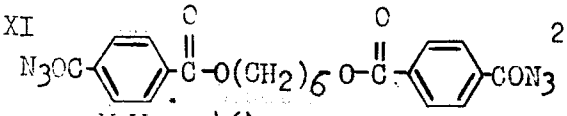
ACID AZIDES THAT HAVE BEEN SYNTHESIZED

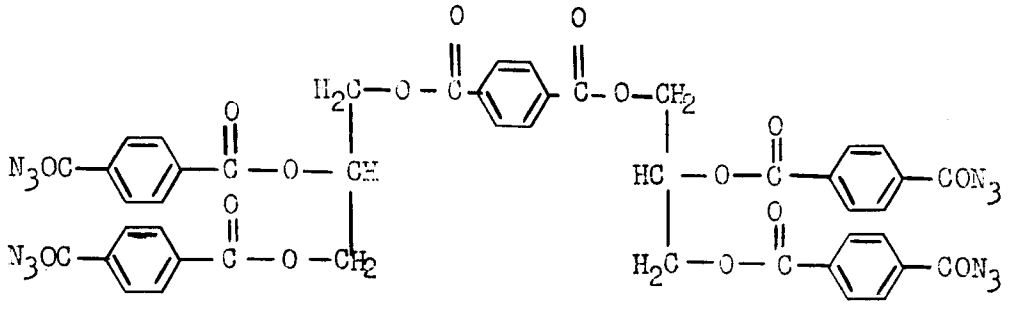
STRUCTURE	AZIDE NAME AND MOL. STRUCTURE	AZIDE FUNCTIONALITY	ISOCYANATE PRODUCED ON RE-ARRANGEMENT	AZIDE N CONTENT (WT. %) TOTAL	RELEASABLE	AZIDE MELTING POINT °F
I	Terephthaloyl Azide  M.W. = 216	2	1,4-Benzene Diisocyanate M.W. = 160 Amine eq. = 80	38.9	25.9	230-232
II	Mesoyl (tri) Azide  M.W. = 285	3	1,3,5-Benzene Triisocyanate M.W. = 201 Amine eq. = 67	44.2	29.5	174
III	Sebacoyl Azide $N_3OC(CH_2)_8CON_3$ M.W. = 252	2	Octamethylene Diisocyanate M.W. = 196 Amine eq. = 98	33.3	22.2	~75 (lit. val. 93)
IV	4,4'-Diphenoyl Azide  M.W. = 292	2	4,4'-Biphenylene Diisocyanate M.W. = 236 Amine eq. = 118	29.8	19.2	259
V	4,4'-Diacyl Azide of Ethylene Glycol Dibenzoate  M.W. = 404	2	4,4'-Diisocyanate of Ethylene Glycol Dibenzoate M.W. = 348 Amine eq. = 174	20.8	13.9	---

REF: ENGINEERING PROCEDURE S.017

TABLE III

ACID AZIDES TO BE SYNTHESIZED

STRUCTURE	AZIDE NAME AND MOL. STRUCTURE	AZIDE FUNCTIONALITY	ISOCYANATE PRODUCED ON RE-ARRANGEMENT	AZIDE N CONTENT (WT %) TOTAL	RELEASABLE
VI	2,6-Naphthaloyl Azide  M.W. = 266	2	2,6-Naphthalene Diisocyanate M.W. = 210 Amine eq. = 105	31.5	21.1
X	4,4'-Diphenyl Methane Diacyl Azide  M.W. = 3D6	2	4,4'-Diphenyl Methane Diisocyanate M.W. = 250 Amine eq. = 125	27.4	18.3
XI	 M.W. = 464	2	--- M.W. = 408 Amine eq. = 204	18.1	12.1
XII	--- M.W. = 1006	4	--- M.W. = 894 Amine eq. = 224	16.7	11.1



D. Azide Synthesis (Continued)

The Structures X, XI, XII represent an attempt to design azide structures to improve on the performance of Structure I, particularly in the areas indicated in Section III.A.1.a., b., f. and (in the case of Structure XII) g.

V. AZIDE SUPPLIERS

This investigation turned out to be much less responsive than anticipated. Many suppliers showed little interest in synthesizing a small number of special unstable azides in research quantities, however, one company was located. Ash-Stevens Incorporated appeared to be suitably capable as determined by our discussions to undertake the synthesizing work. Ash-Stevens Incorporated is a newly formed small company interested in chemical research and small scale chemical synthesis. They expressed an interest in quoting on the custom-synthesized azide chemicals. They claim familiarity with some organic azides.

Specifications and a request for quotation were sent to Ash-Stevens on 10-15-63. A proposal response was received at Goodyear Aerospace on 10-21-63. A coordination meeting was held 10-25-63 and resulted in placing a purchase order which became effective 10-30-63.

VI. PROBLEM AREAS

No unsurmountable problem areas are foreseen at this time.

VII. WORK TO BE PERFORMED DURING THE NEXT REPORTING PERIOD

A. Work will be continued to study formulation variations and their effect upon polymer strength and temperature dependence of strength. This will include use of various polyols.

B. Evaluation methods for new azides will be pursued as far as time will permit. The areas of investigation will include:

1. Determination of shock sensitivity (and friction sensitivity).
2. Thermal decomposition characteristics, time versus temperature.
3. Heat release on decomposition as determined by calorimetry.
4. Solubility in solvents and in prepolymer.
5. Sublimation tendency in high vacuum.
6. Test formulations made with consideration of:
   a. Balance between -OH and produced -NCO.
   b. Available releasable nitrogen for blowing.
   c. Azide decomposition rate, urethane reaction rate and viscosity when blowing.

The above are to be evaluated in terms of density, foam PMT, heat effects, cell structure, post cure and distortion.

C. Attempts will be continued to locate other qualified azide suppliers for back-up.

FIGURE 1

SCHEDULE - RIGIDIZED INFLATABLE SOLAR CONCENTRATOR INVESTIGATION

TASK	1963 OCT	NOV	DEC	JAN	FEB	MAR	1964 APR	MAY	JUN	JUL	AUG	SEPT
I. OPTIMIZATION OF RIGIDIZING MATERIAL												
A. Foam Formulation	■	■	■									
B. Sample Tests	■	■	■	■								
II. DETERMINATION OF MATERIAL CHARACTERISTICS												
A. Screening Tests				■								
B. Specimen Manufacture				■	■	■	■	■	■	■	■	
C. Specimen Tests												
1. Thermal Conductivity				□	□	□	□	□	□	□	□	□
2. Linear Thermal Expansion							□	□	□	□	□	□
3. Stress-Strain				□	□	□	□	□	□	□	□	□
4. Poisson's Ratio							□	□	□	□	□	□
5. Shear				□	□	□	□	□	□	□	□	□
6. Bond Strength							□	□	□	□	□	□
7. Creep				□	□	□	□	□	□	□	□	□
8. Dimensional Stability				□	□	□	□	□	□	□	□	□
9. Ultra-Violet Effects (Bond Strength & Stress-Strain)				□	□	□	□	□	□	□	□	□
10. Reflectance					□	□	□	□	□	□	□	□
D. Structural & Thermal Analysis	□	□	□	□	□	□	□	□	□	□	□	□
III. FABRICATION & TESTING TWO-FOOT MODEL								■	■	■	■	
A. Model Rigidization										■	■	
IV. REPORTS												
MONTHLY	△	△	△	△	△	△	△	△	△	△	△	△
QUARTERLY		△			△			△				
FINAL												△
V. PROJECT ENGINEERING & ADMINISTRATION	■	■	■	■	■	■	■	■	■	■	■	■

LEGEND

△ ■ Planned Work

▲ ■ Work Completed

FIGURE 2

SCHEDULED FORECAST OF MANPOWER UTILIZATION

TASK	1963 OCT	NOV	DEC	1964 JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT	TOTAL
I. FOAM FORMULATION & TESTING													
Cost Center 503-1977.0 Hrs	1	4	4	3									12 M/M
Cost Center 501-2330.0 Hrs	2	5	5	3									15 M/M
Cost Center 515-210.0 Hrs			.5	.5									1 M/M
Cost Center 519-266.0 Hrs			1	1									2 M/M
Total 4783.0 Hrs													
II. MATERIALS TESTING													
Cost Center 503-1055.0 Hrs				.5	.5	1	1	1	1	.5	.5		6 M/M
Cost Center 501-1486.0 Hrs				1.0	1.0	1.5	1.5	1	1	1	1		9 M/M
Cost Center 515- 348.0 Hrs				.2	.2	.2	.2	.3	.3	.3	.3		2 M/M
Total 2889.0 Hrs													
III. FABRICATION & TEST 2-FOOT MODELS													
Cost Center 503-150.0 Hrs							.5	.5					1 M/M
Cost Center 501- 30.0 Hrs									.5	1	.5		2 M/M
Cost Center 515-236.0 Hrs										.2			.2 M/M
Total 416.0 Hrs													
IV. REPORTS													
Cost Center 503-260.0 Hrs		.2	.2	.2	.2	.2	.2	.2	.2	.2	.2	.1	2 M/M
Cost Center 501-470.0 Hrs		.2	.2	.3	.3	.3	.3	.3	.3	.3	.3	.3	3 M/M
Total 730.0 Hrs													
V. PROJECT ENGINEERING, ADMIN. & PLANNING													
Cost Center 503-1300.0 Hrs	.6	.6	.7	.7	.7	.7	.7	.7	.7	.7	.7	.7	8 M/M
Cost Center 501 450.0 Hrs	.2	.2	.2	.2	.3	.3	.3	.3	.3	.3	.3	.3	3 M/M
Total 1750.0 Hrs	4 M/M	10M/M	12M/M	11M/M	3M/M	4M/M	4M/M	4M/M	4M/M	4M/M	4M/M	2M/M	66.2 M/M

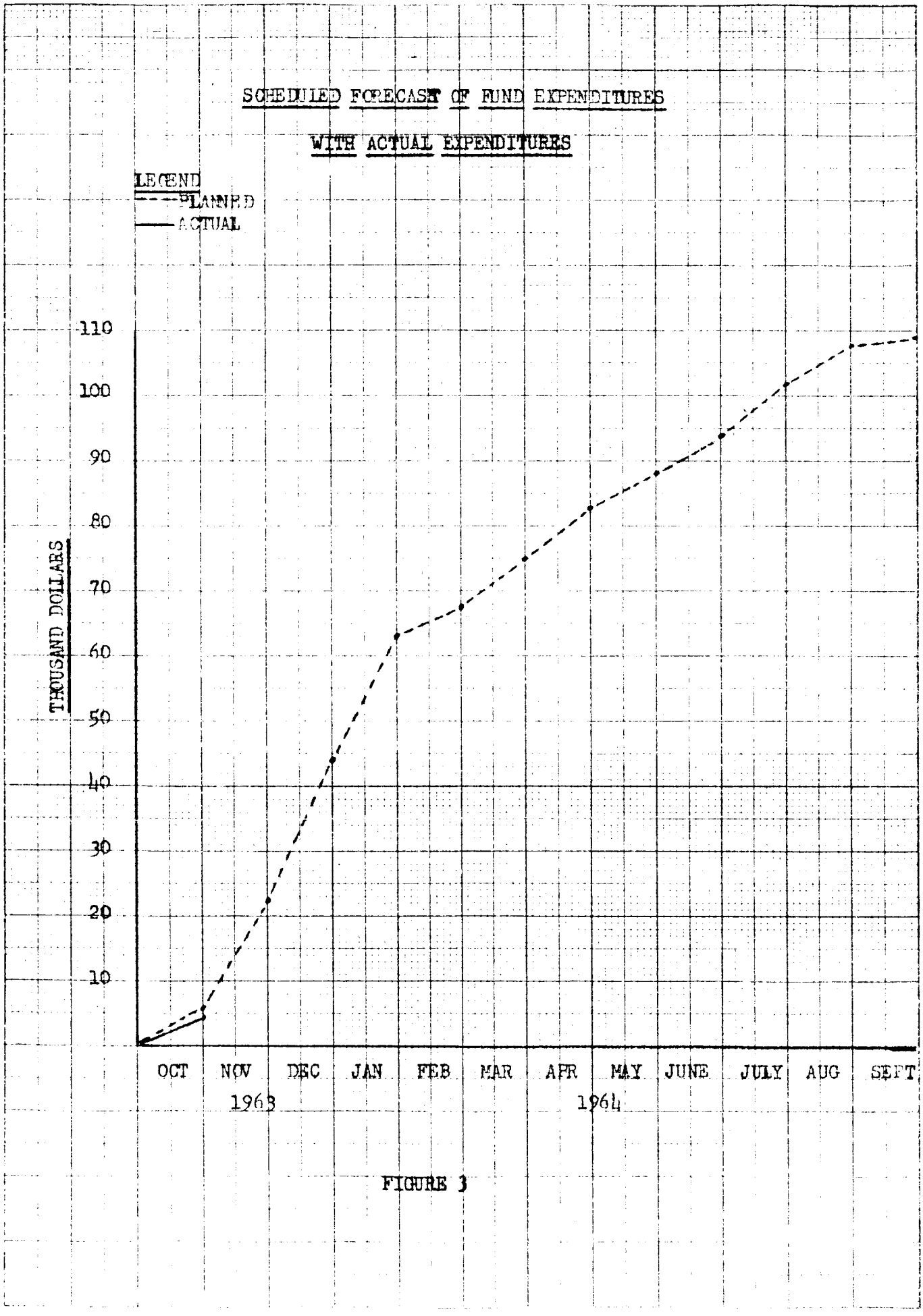

SCHEDULED FORECAST OF FUND EXPENDITURES
WITH ACTUAL EXPENDITURES
LEGEND
PLANNED
ACTUAL
THOUSAND DOLLARS
110
100
90
80
70
60
50
40
30
20
10
OCT
NOV
DEC
JAN
FEB
MAR
APR
MAY
JUNE
JULY
AUG
SEPT
1963
1964

FIGURE 3

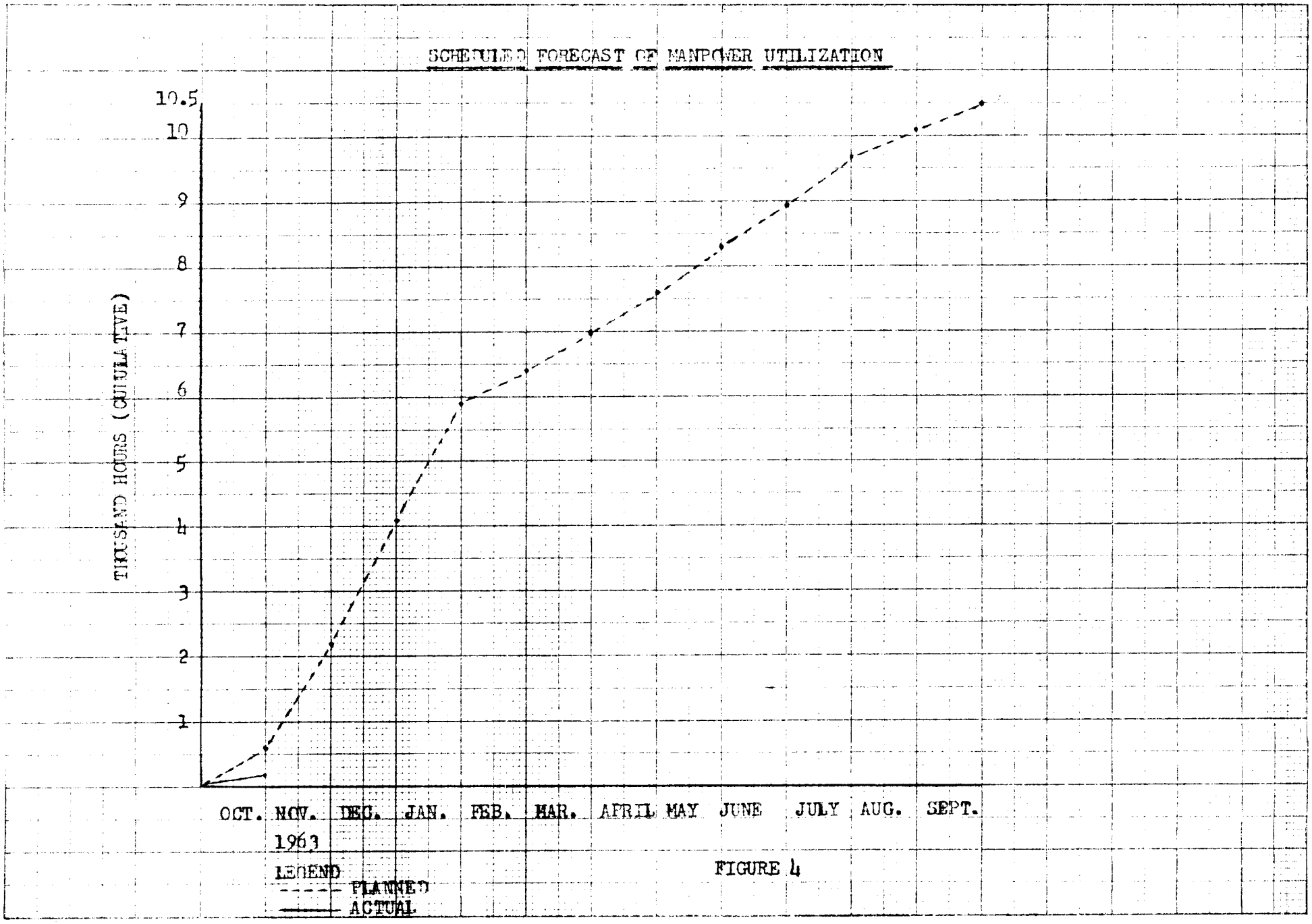

SCHEDULED FORECAST OF MANPOWER UTILIZATION
THOUSAND HOURS (CUMULATIVE)
10.5
10
9
8
7
6
5
4
3
2
1
OCT.
NOV.
DEC.
JAN.
FEB.
MAR.
APRIL
MAY
JUNE
JULY
AUG.
SEPT.
1963
LEGEND
PLANNED
ACTUAL

FIGURE 4